

パラジウム(110)表面における水素吸収の機構

Hydrogen absorption mechanism at the palladium (110) surface

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Hydrogen (H) absorption at palladium (Pd) surfaces is of fundamental importance in many applications such as hydrogen purification, storage, or hydrogenation catalysis. Despite its high technological relevance, the transportation mechanism of H₂ from the gas phase across the surface into the Pd interior is still not properly understood at the atomic level.

The critical surface penetration step is usually envisioned as the diffusion of a surface-adsorbed H atom from the bottom of its chemisorption potential into an empty subsurface interstitial site. However, all currently available *ab-initio* calculations found the energy barrier associated with this diffusion process to be substantially larger than the experimentally observed activation energy of H absorption. A second problem is that the surface-to-subsurface diffusion scenario seems to contradict the observation that chemisorbed D on Pd (100) and (111) surfaces appears to be ‘bypassed’ during absorption and recombinative desorption of gas phase H₂.

In order to clarify the actual penetration mechanism and the role of surface-adsorbed hydrogen, we thus investigated the hydrogen absorption process at a Pd(110) surface with quantitative H depth profiling via ¹⁵N nuclear reaction analysis and thermal desorption spectroscopy with isotope (H,D) labeled surface hydrogen.

We discovered that two distinct H absorption pathways exist on the particular Pd(110) surface that at low temperatures (<145 K) populate two hydride states of different depth distributions and different degrees of surface hydrogen incorporation. A near-surface hydride nucleates at defects in no more than ~4% of the surface area, where the penetration is rapid and locally confined, i.e., isotopic mixing with species adsorbed in the surrounding surface area does not occur. Absorption into the bulk hydride phase, on the other hand, proceeds under complete isotopic mixing of gas-phase and the entire layer of pre-adsorbed surface hydrogen.

Our careful analysis of the isotopic composition of absorbed hydrogen reveals that both absorption routes critically require gas phase molecular hydrogen, involve small activation energies well below 100 meV, and locally replace pre-adsorbed H atoms with the gas phase isotope. To consistently explain these findings we propose a novel ‘hot atom’-mediated exchange/penetration mechanism in which the gas phase supplies dissociated hydrogen atoms in a state of high potential energy that elicit penetration of pre-adsorbed hydrogen into the subsurface and simultaneously reoccupy the vacated chemisorption sites. [1]

[1] S. Ohno, M. Wilde, K. Fukutani, in preparation for Phys. Rev. B.